

PATENT SPECIFICATION

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- (72) Inventors MARVIN F. SMITH, JR. and JOHN P.
 SZYKOWSKI



(54) LUBRICATING OIL COMPOSITIONS

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to lubricating oil compositions containing polymers which act as viscosity index improvers. More particularly, it is concerned with the complementary effect which is obtained when an oil-soluble ester base polymeric additive is used in a lubricant in combination with a second polymeric additive which is essentially hydrocarbon or its aminated-oxidized derivative. The complementary effect is exhibited by the significantly lower viscosity at low temperatures possessed by lubricants containing this combination over that shown by either type of additive when used alone.

The use of polymers as viscosity index (indicated hereafter as V.I.) improvement additives in lubricating oils is old in the art. Polymers comprising C_8 — C_{18} alcohol esters of acrylic or methacrylic acid and derivatives thereof having a number average molecular weight in the range of 50,000 to 500,000 are widely used for this purpose. More recently, Ziegler-Natta copolymers of ethylene and higher alpha-olefins, particularly propylene, and terpolymers of ethylene, a higher alpha-olefin and a non-conjugated diolefin, in a molecular weight range of 10,000 to 200,000 have become known as V.I. improvers.

In general, these ethylene copolymers prepared by Ziegler-Natta type synthesis are less expensive because of low raw material cost, and are frequently more effective on a cost-potency basis than the aforesaid acrylate ester type of V.I. improver.

When free of diluents, the ethylene copolymers have a consistency ranging from heavy viscous syrups in the lower molecular weight ranges to elastomeric solids in the higher molecular weight ranges and are accordingly usually marketed as oil concentrates. Since the polyolefins are essentially hydrocarbon in structure they are compatible with paraffinic or naphthenic oils at concentrations normally used in multi-grade oils and do not separate from solution at low temperatures.

Also proposed as V.I. improvers are nitrogen-containing derivatives of these copolymers obtained by the oxidation of these ethylene copolymers which oxidized derivatives are thereafter reacted with amines to produce nitrogen-containing derivatives.

Polyalkylacrylates vary in their solubility in hydrocarbons and the pour point which they impart to an oil depends on the carbon chain length of the alkyl radical. In the C_8 to C_{12} range where the solidification temperature of the polymers is low, the usual high oxygen content of from 12.5 to 16.2 wt. % limits the solubility of the polymer in hydrocarbons due to its high polarity, and it is best used in synthetic ester lubricants. In the C_{14} to C_{20} range, the solidification temperature rises rapidly and at the upper carbon number range which has the maximum solubility in petroleum lubricants, the products resemble paraffin wax.

Despite considerable studies on the subject, no accurate method is available

for predicting the V.I. change or the compatibility of polymers having diverse structures when mixed in a common solvent such as mineral lubricating oil.

There is considerable prior art on both the ethylene copolymer type of V.I. improver and the ester base polymer type of V.I. improver. Many of the recent patents on the ethylene copolymer V.I. improver made by copolymerizing ethylene with higher olefins, usually propylene, have generalized disclosures that the polymer can be used in conjunction with other additives, including in some cases other V.I. improvers, for example, see U.S. Patents 3,509,056; 3,389,087; 3,326,804; 3,513,095; 3,598,738; and 3,790,480.

More pertinent is U.S. Patent 3,691,078 which teaches an ethylene copolymer as a V.I. improver in lubricating oil, e.g. crankcase oils and automatic transmission fluids (ATF) together with 0.1 to 10 wt. % of certain pour point depressants, such as the reaction product of chlorinated wax and naphthalene; polyalkylmethacrylates; copolymers of alkylaminoalkylmethacrylate and alkylmethacrylate; and polyalkylacrylates. It appears that the commercial practice as exemplified therein is to use only the minimum amount of the polyalkylacrylate V.I. improver as the pour point depressant to be used together with the ethylene copolymer to achieve the desired pour point. In this regard, such a polyalkylacrylate V.I. improver as Acryloid 732 is commercially available as a 35—40 weight percent active concentrate in a paraffinic diluent and is generally used as such in up to 1.2 weight percent (about 0.4—0.5 weight % active polyalkylmethacrylate), to achieve a finished oil pour point —29 to —40°C.

U.S. Patent 3,697,429 discloses ethylene copolymer V.I. improvers of the type included herein together with up to 2% of a pour point depressant of 1,000 to 50,000 molecular weight which pour point depressant is usually characterized by C_{6-18} straight chain groups, including polymers and copolymers of n-alkyl methacrylates, n-alkyl acrylates and copolymers of alkyl fumarate and vinyl acetate.

It is understood by one skilled in the art that lubricating oil additives are blended into base mineral oil stock as a composition consisting of the active compound in a mineral oil diluent.

It has now been discovered that when an ester base type V.I. improver characterized by the presence of oxygen and optionally nitrogen functionality is combined with a second V.I. improver which is essentially hydrocarbon in nature, i.e. an ethylene-higher olefin copolymer or its oxidized and aminated ("polyaminox") derivative, the combination imparts to the lubricating oil a lower pour point and a lower viscosity at low temperatures than when either additive is used alone at the same concentrations as the blend.

The present invention therefore provides a lubricating oil composition comprising a mineral lubricating oil containing from 0.2 to 8 wt. % of a mixture of an oil-soluble ethylene copolymer or its oxidized and aminated derivative, and an oil-soluble ester-base polymer wherein

said oil-soluble ethylene copolymer or derivative has a weight average molecular weight of 10,000 to 800,000 an M_w/M_n ratio less than 10 and a degree of crystallinity not more than 25 wt. %, and comprises 30 to 80 mole % of ethylene, 10 to 70 mole % of a C_3 — C_{18} alpha-olefin;

said oil-soluble ester-base polymer has a number average molecular weight of 20,000 to 1,000,000 and comprises principally C_8 to C_{20} alkyl esters of acrylic acid, methacrylic acid, maleic acid or fumaric acid;

the amount of said ethylene copolymer or derivative is in the range of 0.1 to 2 wt. % of the lubricating composition;

and, the amount of said ester base polymer is in the range of 0.2 to 6.0 wt. %, of the lubricating composition and is 1.5 to 9.0 times the weight of said ethylene copolymer or derivative.

The V.I. improver additive combinations of the invention differ from the aforesaid U.S. Patents 3,691,078 and 3,697,429 in that this invention calls for higher ratios of ester base copolymer V.I. improver to ethylene copolymer (including "polyaminox" derivatives) V.I. improver than that taught in either of the referenced patents.

Ethylene copolymers have been widely taught and used as V.I. improvers in the lubricating oil industry. These ethylene copolymers may be prepared by the polymerization of ethylene with a C_3 to C_{18} , e.g. C_3 to C_8 alpha-olefin, preferably propylene, and optionally one or more copolymerizable additional monomers.

The alpha-olefins may be linear or branched and while a single alpha-olefin is preferable, mixtures of C_3 to C_{18} olefins may be employed. Suitable examples

include propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methyl-1-hexene, 4,4-dimethyl-1-pentene, 4-methyl-1-heptene, 5-methyl-1-heptene, 6-methyl-1-heptene, 4,4-dimethyl-1-hexene, 5,6,5-trimethyl-1-heptene and mixtures thereof.

Ethylene-propylene copolymers are preferred for the purposes of this invention. It is also possible to use a third monomer to form a terpolymer, a fourth monomer to form a tetrapolymer and frequently it is desirable to use a mixture of numerous mono- and/or diolefins to prepare the ethylene copolymer V.I. improver (see U.S. Patents 3,522,180; 3,551,336; 3,598,738; 3,691,078; 3,697,429; and 3,790,480). The third monomer may be one or more C_3 to C_{28} diolefins. These diolefins are also preferably linear but may be branched. The amount of the third monomer contained in the polymer may range from 0 to 10 mole percent, e.g. 0.1 to 5.0 mole percent.

The diolefins which are useful as third monomer for copolymerization with ethylene and propylene include the bicyclic, alicyclic or aliphatic nonconjugated diolefins containing 5—28 carbon atoms, preferably 6—12 carbon atoms. Suitable monomers include 1,5-cyclooctadiene, 1,4-hexadiene, dicyclopentadiene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene, 1,5-cyclododecadiene, 2,4-dimethyl-2,7-octadiene, 3(2-methyl-1-propenyl) cyclopentene, 1,5-octadecadiene, 5-ethylidene-2-norbornene, 1,4-pentadiene; 1,5-hexadiene; 1,6-heptadiene, 1,17-octadecadiene; 5-(5'-hexenyl)-2-norbornene and 2,5-norbornadiene.

The copolymers may be prepared by polymerizing a mixture of the monomer components containing the following components by weight, based upon 100 parts by weight of solvent employed.

TABLE I

Component	Broad Range	Preferred Range	Typical
Ethylene	0.1—10.0	1.0—6.0	3.0—4.7
Higher alpha-olefin	0.1—20.0	1.0—15.0	2.8—4.9
Diolefin	0.0—2.0	0.0—1.0	0
Hydrogen	1×10^{-7} — 1×10^{-2}	1×10^{-6} — 6×10^{-3}	2.35×10^{-4} — 6×10^{-5}

The molar ratios being within the ranges specified for the ethylene copolymers used in the compositions of the present invention.

The monomer mixture may be polymerized to form the desired polymer in the presence of a catalytic amount of a catalyst composition containing as catalyst, a compound of a transition metal and, as cocatalyst, an organometal compound, such as titanium tetrachloride, vanadium oxychloride or vanadium tetrachloride; and diethyl-aluminum chloride, tri-isobutyl-aluminum or ethylaluminum sesquichloride, respectively.

The preferred catalyst composition includes 0.00001 to 0.0001 mole, e.g. 0.00005 mole, of transition metal halide catalyst and 0.00007—0.0007 mole of organoaluminum cocatalyst per 100 parts of solvent employed.

The nonreactive reaction medium may be an aromatic hydrocarbon such as toluene, a saturated aliphatic hydrocarbon such as heptane, pentane, or hexane, or a chlorohydrocarbon such as tetrachloroethylene.

All steps in this reaction should preferably be carried out in the absence of oxygen, moisture, carbon dioxide or other harmful materials. Preferably, all reactants and catalyst are pure and dry and blanketed with inert gas, such as nitrogen or methane.

During polymerization, the reaction mixtures are agitated and maintained at temperatures of -40°C. to 100°C. , e.g., -10°C. to 70°C. , preferably about 30°C. and pressures of 0—1000 psig., preferably 0—300 psig., e.g. 60 psig., during a period of 1—300 minutes, preferably 3—60 minutes, e.g. 15 minutes.

At the end of this period, the reaction mixture is worked up to separate product copolymer.

In the preferred embodiments, the ethylene content of the copolymer is controlled by varying the mole ratio of ethylene to propylene.

Ethylene/alpha-olefin especially ethylene/propylene copolymers useful in the present invention and produced by the aforesaid method will usually have characteristics summarized in the following table:

TABLE II

Property	Broad Range	Preferred Range
Ethylene, mol %	30-80	40-70
Alpha-Olefin, mol %	10-70	25-60
Third Monomer, mol %	0-10	0-5
Degree of crystallinity, wt. percent as determined by the method of Ver Strate and Wilchinsky: Journal of Polymer Science, Vol. 9, p. 127 (1971).	0-25	3-15
$\bar{M}_v \times 10^{-3}$	10-200	20-140
$\bar{M}_w \times 10^{-3}$	5-100	10-70
$\bar{M}_n \times 10^{-3}$	10-800	10-400
\bar{M}_w/\bar{M}_n	10 or below	6 or below

While the ethylene copolymers may be made by direct synthesis in the desired weight average molecular weight range of 10,000 to 800,000 and are desired molecular weight spread, the lower molecular weight polymers may also be made by physically degrading a higher molecular weight polymer as by extruding the polymer under high shear and/or temperature.

POLYOLEFIN A CONCENTRATE

This is a V.I. improver concentrate of 93 weight percent mineral oil, and 7 weight percent of an ethylene copolymer of the following composition:

POLYOLEFIN A

Ethylene mol %	75
Propylene mol %	25
Third Monomer mol %	0
Crystallinity, wt. %	8
$\bar{M}_n \times 10^{-3}$	40
$\bar{M}_w \times 10^{-3}$	80
\bar{M}_w/\bar{M}_n	2

A typical laboratory synthesis of this ethylene copolymer is as follows: Predried ethylene and propylene were fed continuously as gases through calibrated Rotameters (Registered Trade Mark) at 20°C. to a glass reactor provided with an external cooling jacket, mixer, and inlet lines for monomers, solvent, principal catalyst, cocatalyst and hydrogen, and an overflow line to a quench tank. Under

steady-state operating conditions the volume in the reactor was 700 ml. Temperature of the reaction mixture was maintained at the desired level by prechilling the reactor feeds and by circulating chilled water through the jacket upon demand of a sensitive temperature controller.

Hydrogen addition was measured by means of a calibrated Rotameter (Registered Trade Mark). Solvent and catalyst feeds were accurately-metered by means of feed pumps.

Individual solutions of principal catalyst and cocatalyst were prepared by diluting 0.75 millimoles VOCl_3 and 15 millimoles of $\text{Et}_3\text{Al}_2\text{Cl}_3$ to 360 ml. with n-heptane, which had been dried and freed of impurities by percolation through columns filled with Linde 5A molecular sieves and activated silica gel. Similarly purified heptane was used as solvent. Feeds to the reactor are shown in Table III below:

TABLE III

Reactor Feeds:

Heptane Solvent	500 ml/min.
Ethylene	1.38 liters/min.
Propylene	5.47 liters/min.
VOCl_3 solution	7.25 ml/min.
$\text{Et}_3\text{Al}_2\text{Cl}_3$ solution	7.25 ml/min.
Hydrogen	112.0 ml/min.

Reaction Temperature 55°C.

POLYOLEFIN B CONCENTRATE

This is a V.I. improver concentrate of 92 wt. % mineral lubricating oil and 8 wt. % ethylene copolymer of the following composition:

POLYOLEFIN B

Ethylene mol %	54
Propylene mol %	46
Third Monomer mol %	0
Crystallinity, wt. %	0
$\overline{M}_n \times 10^{-3}$	60
$\overline{M}_w \times 10^{-3}$	120
$\overline{M}_w/\overline{M}_n$	2

A typical laboratory synthesis of this copolymer may be carried out in the same general manner as used to prepare Polyolefin A, but varying the ethylene and propylene feeds. Both Polyolefins A and B are conventional V.I. improvers.

"Polyaminox" Derivatives of the Ethylene Copolymers and Terpolymers

The above-described ethylene copolymers are oxidized and thereafter reacted with amines to produce the "polyaminox" derivatives (the aminated oxidized derivatives of the ethylene copolymer additive earlier discussed). Oxidation of hydrocarbon polymers is well-known.

Reaction of oxidized ethylene copolymer with nitrogen-containing compounds, such as amines, is also well known, e.g. see U.S. Patents 3,076,791 and 3,785,980.

Oxidation of hydrocarbon polymers prior to the amine reaction can be carried

out by numerous processes including hydroperoxidation of ethylene-propylene copolymers (U.S. Patent 3,785,980) and mechanical degradation while heating in air (U.S. Patent 3,769,216).

5 Particularly useful herein are ethylene copolymers oxidized in mineral oil and subsequently reacted with amines as described in United Kingdom Patent Application Number 1,511,501 13898/75 filed April 4, 1975. In this process, a wide variety of mineral lubricating oils may be used as solvent for the polymer-oil solutions to be oxidized. The oils may range in viscosity from 5 to 1000 SUS at 38°C., most preferably 80 to 200 SUS at 38°C. They may be straight-run distillates 10 in the lubricant range, e.g. boiling above 315°C., or may have been further refined. Also suitable are synthetic hydrocarbon oils in the lubricant range made by polymerization, oligomerization, alkylation of aromatics with olefins and the like. Preferred are oils having a sulfur content less than 0.25 weight percent, a nitrogen content less than 25 micrograms per ml., and an aromatic content less than 30 15 weight percent.

Oxidation of the copolymers and terpolymers dissolved in the oil is conveniently carried out in a stirred reactor with air, or air prediluted with an inert gas such as nitrogen or carbon dioxide so as to minimize explosion hazards. The air, or diluted air, may be introduced into the oil-polymer solution in a finely divided state at a temperature in the range of 80°C. to 300°C., preferably 100°C. to 230°C. with rapid agitation of the reactor contents. 20

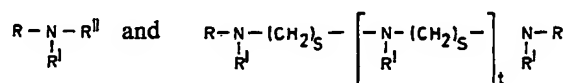
In general, in the range of 0.5 to 90, e.g. 4 to 60 weight percent, of the oil-polymer solution will be polymer. Usually, about 20 to 60 weight percent of the solution will be polymer when the polymer is of low molecular weight, e.g. with a number average molecular weight (M_n) less than 20,000. For polymers with M_n 25 equal to or greater than 20,000, the preferred concentrations are in the range of 4 to 20 weight percent polymer, based on the total weight of the oil-polymer solution.

Oxidation of the oil-polymer solution is conducted for a time sufficient to impart to the solution a combined oxygen content of about 0.01 to 10.0, e.g. 0.1 to 8, preferably 0.1 to 5.0 weight percent, depending on the composition of the oil, the polymer and the concentration of polymer in solution. 30

As used herein, such terms as "oxidized", or "oxidized oil polymer solution" indicate that air or oxygen containing gas is used for the oxidation, and precludes the use of other oxidative reagents such as ozone. 35

Useful amine compounds for condensation with the oxidized polymer-oil solutions to form the "polyaminox" products of this invention include amines of 2 to 60, e.g. 3 to 20, total carbon atoms and about 1 to 12, e.g. 1 to 6, nitrogen atoms in the molecule, which amines may be hydrocarbyl amines or may include other groups, e.g. 1 to 4 hydroxyl groups, alkoxy groups, amide groups and imidazoline groups. 40

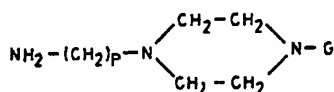
Preferred amines are aliphatic, saturated amines, and include those of the general formulae:



45 wherein R, R' and R'' are independently selected from hydrogen; C₁ to C₁₂ straight or branched chain alkyl radicals; C₁ to C₁₂ alkoxy substituted C₂ to C₆ alkylene radicals; C₂ to C₁₂ hydroxy- or amino-alkylene radicals; and C₁ to C₁₂ alkylamino substituted C₂ to C₆ alkylene radicals; s is 2 to 6, preferably 2 to 4; and t is 0 to 10, preferably 2 to 6.

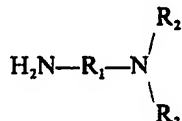
50 Examples of suitable amine compounds represented by the above include: n-octyl-amine; n-dodecyl-amine; di-(2-ethylhexyl)-amine; 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; diethylene-triamine; triethylene-tetramine; tetraethylene-penta-amine; 1,2-propylene-diamine; di-(1,2-propylene)-triamine; di-(1,3-propylene)-triamine; N,N-dimethyl-1,3-diaminopropane; N,N-di-(2-aminoethyl)-ethylene-diamine; N,N-di-(2-hydroxy-ethyl)-1,3-propylene-diamine; 3-dodecyl-oxy-propylamine; N-dodecyl-1,3-propane-diamine; diethanol-amine; morpholine; trishydroxymethyl-aminomethane (THAM) and diisopropanol amine. 55

60 Still other useful amine compounds include: alicyclic diamines such as 1,4-di-(aminomethyl)-cyclohexane and heterocyclic nitrogen compounds such as imidazolines and N-aminoalkyl-piperazines of the general formula:



wherein G is selected from hydrogen and omega-aminoalkylene radicals of from 1 to 3 carbon atoms; and p is an integer of 1 to 4. Examples include 2-pentadecyl-imidazoline; N-(2-aminoethyl)-piperazine; N-(3-aminopropyl)-piperazine; and N,N'-di(2-aminoethyl)-piperazine.

Other alkylene amino compounds that can be used include dialkylamino-alkyl-amine such as dimethylamino-ethylamine, dimethylamino-propyl-amine and methylpropylamino-aryl-amine. These may be characterized by the formula:



wherein R₁ is an alkylene radical, e.g., an ethylene, propylene, or butylene radical, and R₂ and R₃ are C₁ to C₃ alkyl radicals.

Commercial mixtures of amine compounds may advantageously be used for the preparation of the "polyaminox" compositions of this invention. For example, one process for preparing alkylene amines involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene amines wherein pairs of nitrogen atoms are joined by alkylene groups, forming such compounds as diethylene triamine, triethylene tetra-amine, tetraethylene penta-amine and isomeric piperazines. Low cost poly(ethylene amine) compounds having a composition approximating tetraethylene penta-amine are available commercially under the trade names Polyamine H, Polyamine 400, (PA-400) and Polyamine 500 (PA-500). Similar materials may be made by the polymerization of aziridine, 2-methylaziridine and azetidine.

The more important alkylene polyamine or aliphatic polyamine compound used in this invention can be broadly characterized as an alkylene amino compound containing from 2 to 12 nitrogen atoms where pairs of nitrogen atoms are joined by alkylene groups of from 2 to 4 carbon atoms.

Reaction of the amine compound with the polymer solution takes place readily at a temperature in the range 40°C. to 300°C., preferably at a temperature in the range 100°C. to 200°C. Accordingly, after the oxidation of the oil-polymer solution has reached the desired level, the required amount of amine compound, usually in the range 0.1 to 4.0 wt. % based on the weight of the polymer, may be added with mixing and the reaction mixture maintained at the required temperature while removing any water that forms. The time for completion of the reaction of the amine compound with the oxidized oil-polymer solution is about 15 minutes to about 50 hours depending on temperature, degree of mixing and reactivity of the amine compound. The final aminated product will usually contain in the range 0.03 to 5, e.g. 0.1 to 3.0, wt. % nitrogen, based on the total weight of the aminated polymer.

POLYOLEFIN C CONCENTRATE

This V.I. improver consists of about 92 wt. % mineral oil and 8 wt. % of the "polyaminox" derivative of the oxidized in oil mixture of 1528 grams of an ethylene/propylene copolymer (about 75 mole percent ethylene) having a \bar{M}_w of about 130,000 and 1528 grams of an ethylene/propylene copolymer (about 56 mole percent ethylene) having a \bar{M}_w of about 195,000 each polymer having the properties required of the oil-soluble ethylene copolymer or derivative of the compositions of the invention. Each copolymer was individually dispersed in mineral oil and oxidized by passing air through the mixture at elevated temperatures. The copolymer of about 75 mole percent ethylene was oxidized at 340°F. for 11½ hours. The copolymer of about 56 mole percent ethylene was oxidized at 340°F. for 21 hours. Each showed infrared (IR) absorptions at 1720 cm⁻¹ in a 5 mm cell of 0.208 and 0.244, respectively. To this mixture of oxidized ethylene-propylene copolymers having a \bar{M}_w of about 90,000, 4.6 grams of diethylene triamine was added at between 25°C. and 100°C. after nitrogen.

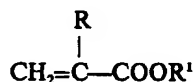
sparging. The temperature was raised to and kept at about 160°C. for 2-2/3 hours under an inert atmosphere of nitrogen and thereafter cooled to 120°C. whereupon it was bottled. This "polyaminox" concentrate showed a nitrogen content of 0.046 wt. %.

The Ester Base Polymers

These V.I. improving, oil-soluble ester base polymers will have number average molecular weights in the range of 20,000 to 1,000,000, preferably 50,000 to 500,000 and most preferably, 50,000 to 200,000. These ester base polymers are derived principally, e.g., 80 wt. % or more of the total polymer, from C_8 to C_{20} , preferably C_{12} to C_{18} , alkyl esters of acrylic acid, methacrylic acid, maleic acid or fumaric acid. V.I. polymers of this ester base type are well-known in the art and are usually made by free radical initiation, e.g. using a peroxide, in a solvent.

Such esters from which the polymer is essentially derived include alkyl acrylate, alkyl methacrylate, and dialkyl fumarate and dialkyl maleate.

The most common of these V.I. improvers are polymers of acrylic esters represented by the formula

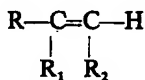


wherein R represents hydrogen or methyl and R' represents an oil solubilizing group, especially an alkyl group of 8 to 24 carbon atoms. The alkyl group may be essentially straight chain and preferably contains 12 to 18 carbon atoms although methyl and ethyl branching can be tolerated. Representative polyacrylic and polymethacrylic esters that promote oil solubility comprise octyl, decyl, isodecyl, dodecyl, isododecyl, myristyl, cetyl, stearyl, eicosyl and tetracosyl polyacrylates and polymethacrylates. The term "acrylic ester" in this invention includes both acrylates and methacrylates. Mixtures of both alkyl acrylates and alkyl methacrylates may be used.

Lower alkyl acrylic esters having alkyl groups smaller than 8 carbon atoms and derived from acrylic or methacrylic acid may be used in combination with the previously mentioned higher acrylic esters. The presence of small alkyl groups in the copolymers may help improve such properties as the viscosity index. Typical lower acrylic esters are methyl, ethyl, propyl, butyl, amyl, and hexyl acrylates and methacrylates. These lower alkyl acrylic esters may be employed in amounts ranging from 0 to 25 mole %, based on the total ester content.

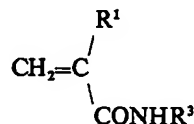
In addition to the aforementioned acrylic esters, there may be used to form the backbone, in minor amounts, one or more other free radical polymerizable monoethylenically unsaturated compounds, particularly monovinylidene compounds, i.e. those having one $\text{CH}_2=\text{C}$ group in their structure, such as vinyl esters, e.g. vinyl acetate, styrene and alkyl-styrenes, vinyl alkyl ethers, e.g. vinyl butyl ether, vinyl dodecyl ether and vinyl octadecyl ether.

In addition, nitrogen-containing monomers can be copolymerized with the foregoing monomers, said nitrogen-containing monomers include those represented by the formula:

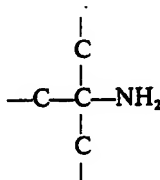


wherein R_1 and R_2 can be hydrogen and/or alkyl radicals and R is a 5- or 6-membered heterocyclic nitrogen-containing ring and which contains one or more substituent hydrocarbon groups. In the above formula, the vinyl radical can be attached to the nitrogen or to a carbon atom in the radical R. Examples of such vinyl derivatives include 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, 2-ethyl-5-vinylpyridine, 4-methyl-5-vinylpyridine, N-vinylpyrrolidone, 4-vinylpyrrolidone and the like.

Other monomers that can be included are the unsaturated amides such as those of the formula:



wherein R¹ is hydrogen or methyl, and R³ is hydrogen or an alkyl radical having up to 24 carbon atoms. Such amides are obtained by reacting acrylic acid or a low molecular weight acrylic ester with an amine such as butylamine, hexylamine, tetrapropylene-amine, cetylamine and tertiary-alkyl primary amines. The tertiary-alkyl primary amines referred to conform to the characterizing structure



wherein a tertiary carbon atom, i.e., one devoid of hydrogen atoms is bonded to a primary amino radical, i.e. —NH₂. Such tertiary-alkyl primary amines should contain at least 6 and generally not more than 24 carbon atoms in the tertiary-alkyl substituent. In most instances, the tertiary-alkyl substituent will contain from 10 to 24 carbon atoms. Specific examples of tertiary-alkyl primary amines useful for the purposes of this invention include tertiary-octyl primary amine, tertiary-decyl primary amine and tertiary-hexadecyl primary amine, tertiary-eicosyl primary amine and tertiary-triacontyl primary amine. It is not necessary to use a single tertiary-alkyl primary amine; in fact, it is generally more convenient to use a commercial mixture of such amines wherein the tertiary-alkyl substituent contains from 10 to 24 carbon atoms. A typical mixture of such commercial tertiary-alkyl primary amines, for example, consists of tertiary-alkyl primary amines containing from 12 to 14 carbon atoms, said mixture averaging about 12 carbon atoms per amine molecule.

Still other monomers that can be included are amides and mixed amide-esters of the vinyl monocarboxylic and dicarboxylic acids mentioned previously. These monomers and the earlier discussed lower alkyl acrylic esters, monovinylidene compounds, nitrogen containing monomers and unsaturated amides may individually or collectively be employed in total amounts ranging from 0 to 25 mole percent, based on the total ester content.

The following specific ester base polymers were used in the examples of the invention.

POLYESTER A CONCENTRATE

This was a V.I. improver concentrate of 63 wt. % oil and 37 wt. % of an ester base copolymer consisting of a major proportion of about 95 mole % of C₁₀ to C₂₀ alkyl methacrylate monomer with alcohols containing an average carbon number of 14.5 and a minor proportion (about 5.0 mole %) of an amino-methacrylate copolymerized with the aid of a free radical catalyst. The copolymer has a nitrogen content of 0.2 wt. % and a number average molecular weight in the range of 50,000 to 100,000.

POLYESTER B CONCENTRATE

This was a commercial V.I. improver concentrate (sold as Acryloid 953 by Rohm and Haas) of 62 wt. % oil and 38 wt. % of ester base copolymer consisting of a major proportion of C₁₀ to C₁₈ alkyl (average number of carbons is 12—15 range) methacrylate monomers and a minor proportion of a nitrogen-containing monomer which copolymer upon chemical analysis contains about 0.2 wt. % nitrogen with a number average molecular weight between 50,000 and 100,000.

POLYESTER C CONCENTRATE

This was a commercial V.I. improver additive concentrate of about 66 wt. % oil and about 34 wt. % of a terpolymer sold as LZ 3702 by Lubrizol Corporation. This additive consists of styrene, dialkyl maleate and a minor proportion of a nitrogen-containing monomer which terpolymer upon chemical analysis contains about 0.15% nitrogen with a number average molecular weight between 50,000 and 100,000.

POLYESTER D CONCENTRATE

This was a commercially available concentrate of 60 wt. % oil and 40 wt. % polyalkyl methacrylate having the properties required of the oil-soluble ester base

polymer used in the composition of this invention and sold as Acryloid 732 by Rohm and Haas Chemical Co.

The molecular weights for the polyester concentrates are all set forth as number average (M_n) which are calculated through the technique of membrane osmometry using a 3-Stabin Dohrmann Semi-Automatic Recording Osmometer with toluene as a solvent and measured at about 35°C.

The polymer blends of the invention are 1.5 to 9.0 and optimally 1.5 to 4 parts by weight of the ester base copolymer per part by weight of the ethylene copolymer and/or its "polyaminox" derivative.

The polymer mixtures of this invention can be incorporated in lubricating oil compositions, e.g. automotive crankcase oils, in concentrations within the range 0.1 to 2 weight percent ethylene copolymer and/or "polyaminox" derivative (on an active basis) based on the weight of the total compositions, whereas for the ester base copolymer concentrations within the range 0.2 to 6 weight percent is appropriate.

The overall concentration of the mixture in the lubricating oil composition will be from 0.2 wt. % to 8 wt. % of the total composition.

In the above lubricating oil, other conventional additives may also be present, including dyes, pour point depressants, antiwear agents, e.g. tricresyl phosphate, zinc dialkyl dithiophosphates of 3 to 8 carbon atoms, antioxidants such as phenyl alpha-naphthylamine, tert. octylphenol sulfide, bisphenols such as 4,4'-methylene-bis-(2,6-di-tert. butyl phenol), as well as ashless dispersants or detergents, such as polyisobutenyl-succinimides and pentaerythritol esters of polyisobutenyl succinic anhydride.

EXAMPLES

The following mineral lubricating oils were used for compounding the lubricants which are then tested for viscosity as shown in the following tables.

Solvent Neutral S—70 A solvent extracted, hydrofined oil having a viscosity of 99°C. of 36.5 SUS; viscosity at 38°C. of 74 SUS; viscosity index of 78; and a pour point of -29°C.

Solvent Neutral H—75 A solvent extracted, hydrofined oil having a viscosity at 99°C. of 36.8 SUS, viscosity at 38°C. of 72 SUS; viscosity index of 108; and a pour point of -18°C.

Solvent Neutral H—100 A solvent extracted oil having a viscosity at 99°C. of 40.5 SUS, viscosity at 38°C. of 110 SUS; viscosity index of 106 and a pour point of -18°C.

Solvent Neutral H—150 A solvent extracted oil having a viscosity at 99°C. of 44 SUS, viscosity at 38°C. of 155 SUS; viscosity index of 107; and a pour point of -18°C.

Solvent Neutral H—110 A blend of eight volume parts of Solvent Neutral H—100 with two volume parts of Solvent Neutral H—150. All viscosity measurements are by ASTM Method D—445.

A series of experiments was run in which blends of the various polyolefin and ester based polymers were made in the oils listed above by addition of a polymer concentrate of each to the oil with stirring and heating at about 60—66°C. until solution was complete. The Brookfield viscosities of the blends in centipoises were then determined at -40°C. The results obtained are given in Table IV.

TABLE IV
Viscosities of Polymer Blends

Example Number	Polymer type and Concentration (Wt.%)*		Oil Type	Viscosity 10 ³ cP@-40°C
	Polyolefin	Polyester		
1	0.83% B	—	S-70	solid
2	0.42% B	—	S-70	solid
3	0.72% A	—	S-70	solid
4	0.36% A	—	S-70	solid
4-A	0.36% C	—	S-70	solid
5	—	3.9% A	S-70	solid
6	—	2.0% A	S-70	21
7	—	3.9% A	S-70	146.0
8	—	2.0% B	S-70	9.5
9	—	3.5% C	S-70	83.0
10	—	1.8% C	S-70	8.9
11	0.42% B	2.0% A	S-70	64.0
12	0.36% A	2.0% B	S-70	17.5
13	0.36% A	1.8% C	S-70	15.8
13-A	0.36% C	1.8% C	H-75	17.2
14	0.36% A	2.0% A	H-75	32.3
14-A	0.36% C	2.0% A	H-75	67.6
15	0.72% A	—	H-75	solid
16	0.36% A	—	H-75	solid
17	—	3.9% A	H-75	solid
18	—	2.0% A	H-75	92.2
19	0.36% A	2.0% A	H-75	85.7
20	0.70% A	—	H-100	solid
20-A	0.70% A	—	H-100	solid
21	0.35% A	—	H-100	solid
22	—	3.8% A	H-100	solid
23	—	1.9% A	H-100	109
24	—	3.4% A	H-100	solid
25	—	1.7% C	H-100	80.8
26	0.35% A	1.9% A	H-100	128.6
26-A	0.35% C	1.9% A	H-100	176.2
27	0.35% A	1.7% C	H-100	98.2
27-A	0.35% C	1.7% C	H-100	105.0
28	—	3.8% B	H-100	solid
29	0.35% A	1.9% B	H-100	63.0
30	0.70% A	—	H-110	solid
31	—	3.8% A	H-110	solid
32	0.35% A	1.9% A	H-110	134.0

* Active polymer in weight percent

Comparison of the results obtained in Example 11 with 2 and 6; 12 with 4 and 8; 13 and 13-A with 4, 4-A and 10; 14 and 14-A with 4, 4-A and 6; 19 with 16 and 18; 26-27-A with 19-25, shows the complementary effect obtained with the combination of a polymeric polyolefin and polyester additive compared to either used alone.

Extending these data, experiments were run in which blends of Polyester Polymer A and Polyolefin A were made at various concentrations in Solvent Neutral Oil S-70 and the viscosities of the blends determined at several temperatures. In order to approximate the properties of a finished automatic transmission fluid a detergent-inhibitor package was added to each blend to provide 2 wt. % of the detergent-inhibitor compounds. The detergent-inhibitor combination comprised a mixture of a polyisobutenyl-succinic anhydride-tetraethylene pentamine condensation product; a phosphosulfurized terpene; a zinc dialkyl-dithiophosphate; an ethoxylated alkyl-phenol; an aryl-naphthylamine; and a silicone antifoamant. The results obtained are shown in Table V.

TABLE V

Viscosities of a Blend of Polyester A
and Polyolefin A in S-70 Neutral Oil

Example Number	Wt. % Polyester A in Blend	Wt. % Polyolefin A Blend	Wt. % Total Polymer in Blend	SUS @ 99°C.	cP @ -18°C.	10 ³ cP @ -40°C.
33	—	0.74	0.74	53.5	805	solid
34	2.80	—	2.80	55.0	—	74.3
35	3.40	—	3.40	59.9	—	200
36	1.60	0.29	1.89	52.4	—	14.4
37	1.95	0.36	2.31	57.6	890	20.0
38	1.50	0.56	2.06	60.3	990	43.0
39	2.33	0.44	2.77	63.0	—	28.0

The data in Tables IV and V indicate that the polyolefins possess greater thickening power than the polyfunctional VI improvers when measured at the same concentration and that mixtures of the polyolefins and polyfunctional compounds according to the invention show lower viscosities at low temperatures than equivalent concentrations of either V.I. improver.

A further advantage in the case of mixtures aside from the lower cost of the polyolefins compared to the polyfunctional compounds is the lower pour point and improved fluidity of blends at lower temperatures. The improved fluidity results in better lubricant dispensibility from a container which has remained at low temperatures for a period of time. Table VI gives the results of a number of blends illustrating these properties.

TABLE VI

Viscosities of a Blend of Polyolefin B
and Polyester B in an SAE 10W-30 Oil

Example Number	Wt. % Polyolefin B in Blend (d)	Wt. % Polyester D in Blend (d)	Kin. Vis. cS @ 99°C.	Centipoises @ -18°C.	ASTM Pour Point °C.	Fluidity test flow time, seconds @ -29°C. (c)
40	0.0	0.0	6.02	1,600 (b)	-7 (a)	—
41	0.0	2.4	11.12	1,970	-34	8.8
42	0.7	0.0	11.55	1,800 (b)		
43	0.6	0.4	10.94	1,830	Below -37	7.0
44	0.5	0.8	10.91	1,880	Below -37	5.8

(a) pour point without pour depressant addition.

(b) with 0.5% addition of a pour depressant comprising a copolymer of equal moles of a Di C₁₀-C₂₀ alkyl fumarate and vinyl acetate, with a molecular weight of about 15,000 (number average).

(c) Fluidity Test Flow Time is equal to number of seconds for a sample of oil held at -29°C. for 64 hours in a ASTM D97 jar to flow one-half inch when the jar is tilted 90°.

(d) Blend also contains base oil and other detergent-inhibitor additives necessary for lubrication of automobile engines.

Lower viscosities at low temperatures are important for lubricants such as automotive transmission fluid, automotive engine oils and multigrade gear oils since such fluids must meet certain maximum levels at specified temperatures tailored to each lubricant type and grade. Lubricant formulations strive for certain minimum viscosities at high temperature and the aforementioned maximum viscosities at low temperature to yield the desired viscometric performance. This invention provides a means for meeting such requirements economically; particularly for operation temperatures ranging from -60°F. to +15°F.

Such useful automatic transmission fluid is represented by the following formulation:

5

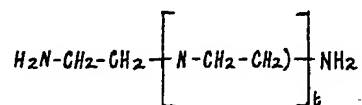
10

Additive type	Compound	Amount %
Diluent/base oil	Mineral Oil (100 neutral)	94.2 (or balance)
Viscosity Index improvers	Polyolefin A Polyester A	0.25 0.75
Corrosion Inhibitor	phosphosulfurized terpene	0.3
Oxidation Inhibitor	phenyl-alpha-naphthylamine	0.3
Friction Modifier	calcium oleate	0.4
Seal swellant	dihexyl phthalate	2.0
Dispersant	polyisobutenyl-succinimide	1.5
Antiwear agent	zinc dialkyl dithiophosphate	0.3
Anti-foamant	polydimethyl-siloxane	0.002

All percentages are in volume percent except for the anti-foamant and viscosity index improvers, which are given as weight percent.

WHAT WE CLAIM IS:—

- 5 1. A lubricating oil composition comprising a mineral lubricating oil containing from 0.2 to 8 wt. % of a mixture of an oil-soluble ethylene copolymer or its oxidized and aminated derivative, and an oil-soluble ester-base polymer wherein
 - 10 said oil-soluble ethylene copolymer or derivative has a weight average molecular weight of 10,000 to 800,000, an $\overline{M}_w/\overline{M}_n$ ratio less than 10 and a degree of crystallinity not more than 25 wt. %, and comprises 30 to 80 mole % of ethylene, 10 to 70 mole % of a C_3-C_{18} alpha-olefin;
 - 15 said oil-soluble ester-base polymer has a number average weight of 20,000 to 1,000,000 and comprises principally C_8 to C_{20} alkyl esters of acrylic acid, methacrylic acid, maleic acid or fumaric acid;
 - 20 the amount of said ethylene copolymer or derivative is in the range of 0.1 to 2 wt. % of the lubricating composition;
 - 25 and the amount of said ester base polymer is in the range of 0.2 to 6.0 wt. % of the lubricating composition and is 1.5 to 9.0 times the weight of said ethylene copolymer or derivative.
 2. A lubricating oil composition according to claim 1, wherein said C_3-C_{18} alpha-olefin is propylene.
 3. A lubricating oil composition according to claim 2, wherein said first polymer is oxidized as hereinbefore described and aminated derivative and contains from 0.03 to 5 wt. % nitrogen and has been prepared by oxidizing a lubricating oil solution of a copolymer of ethylene and propylene, at a temperature of 80°C. to 300°C. and for a time sufficient to impart to said solution a combined oxygen content of 0.01 to 10.0 wt. % oxygen, based on the weight of said oil solution, and then aminating said oxidized oil solution with a polyethylene polyamine of the formula
 - 30



wherein t is 2 to 6.

4. A lubricating oil composition according to claims 1—3, wherein said ester base polymer consists essentially of alkyl methacrylate residues.

5. A lubricating oil composition according to claim 1 substantially as hereinbefore described with reference to Examples 11—14A, 19, 26—27A, 29, 32 and 36—39.

K. J. VERYARD,
15, Suffolk Street,
London, S.W.1.
Agent for the Applicants.

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